

U. S. PTO  
JC518 06/02/98

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

The Commissioner of Patents & Trademarks  
Washington, D.C. 20231  
Attn: Box Patent Application  
Sir: This is a request for filing a

Docket No. ATOCL 67 D1  
Prior Application: 08/738,768  
Examiner: I. Zemel  
Art Unit: 1505

Continuation  
 Divisional

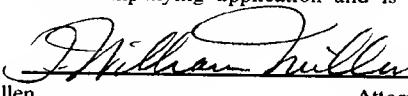
Of pending prior application Serial No. 08/738,768 filed on October 28, 1996 of Chris BERTELO et al., for "Impact Additive of the Core/Shell Type for Thermoplastic Polymers".

1.  Enclosed are five-one (51) pages of the specification including claims and zero (0) sheets of drawings.
2.  Enclosed is a copy of the oath or declaration as originally filed in Serial No. 08/738,768 on October 28, 1996, in accordance with 37 C.F.R. §1.63(d).
3.  The filing fee is calculated below:

FOR	NUMBER FILED	NUMBER EXTRA	RATE	FEE
<b>TOTAL CLAIMS</b>	46 - 20	26	\$22	\$ 572.00
<b>INDEPENDENT CLAIMS</b>	2 - 3	0	\$82	0
<input type="checkbox"/> MULTIPLE DEPENDENT CLAIM PRESENTED				
<input type="checkbox"/> Small Entity Status Claimed under 37 CFR 1.9 and 1.27			<b>BASIC FEE</b>	790.00
Statement(s): <input type="checkbox"/> Attached <input type="checkbox"/> Filed in Parent			<b>TOTAL FILING FEE</b>	\$ 1,362.00

4.  The amount of \$ 1,362.00 is included in the attached check.
- If a check is not attached, authorization is given to charge the amount indicated in the above sentence to Deposit Account No. 13-3402; two copies of this page being attached for this purpose.
- Please charge my Deposit Account No. 13-3402 in the amount of \$ \_\_\_\_\_, two copies of this sheet are attached.
- The Commissioner is hereby authorized to charge any deficiencies or credit any overpayment in payment of the following fees associated with this communication or otherwise due during the pendency of this application to Deposit Account No. 13-3402.
  - Any filing fees under 37 CFR §1.16 for the presentation of extra claims.
  - Any patent application processing fees under 37 CFR §1.17.
- Cancel in this application original claims \_\_\_\_\_ of the prior application before calculating the filing fee.
- Amend the specification by inserting before the first line the sentence:  
-- This is a  continuation,  division, of application Serial No. 08/738,768 filed October 28, 1996. --
- Priority of application No. 95/12706 filed on 27 October 1995 in France is claimed under 35 U.S.C. §119.
- The certified copy has been filed in prior application Serial No. 08/738,768 filed October 28, 1996.
- The prior application is assigned of record to ELF ATOCHEM NORTH AMERICA INC.
- The power of attorney in the prior application is to I. William Millen, Reg. No. 19,544; John L. White, Reg. No. 17,746; Anthony J. Zelano, Reg. No. 27,969; Alan E.J. Branigan, Reg. No. 20,565; John R. Moses, Reg. No. 24,983; Harry B. Shubin, Reg. No. 32,542; Diana Hamlet-King, Reg. No. 33,302; Richard J. Traverso, Reg. No. 30,595; Richard E. Kurtz, Reg. No. 33,936; John A. Sopp, Reg. No. 33,103; and Richard M. Lebovitz, Reg. No. 37,067.
  - a. The power appears in the original papers in the prior application.
  - b. Address all future communications to MILLEN, WHITE, ZELANO & BRANIGAN, P.C.
- A preliminary amendment is enclosed.
- An Information Disclosure Statement is enclosed.
- Incorporation By Reference.  
The entire disclosure of the prior application, from which a copy of the oath or declaration is supplied under Box 2, is considered as being part of the disclosure of the accompanying application and is hereby incorporated by reference therein.

Date: June 2, 1998

  
I. William Millen  
MILLEN, WHITE, ZELANO & BRANIGAN, P.C.

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Divisional Application of : **Box PATENT APPLICATION**  
Chris BERTELO et al. : Examiner: I. Zemel  
Serial No.: Unknown : (Anticipated)  
Filed: June 2, 1998 : Group Art Unit: 1505  
(Anticipated)

For: **IMPACT ADDITIVE OF THE CORN/SHELL TYPE FOR  
THERMOPLASTIC POLYMERS**

**Preliminary Amendment**

Assistant Commissioner for Patents  
Washington, D.C. 20231

Sir:

Prior to examination, Applicants wish to amend the above-identified application as indicated below.

**IN THE CLAIMS:**

**Cancel claim 35, without prejudice to or disclaimer of the subject matter contained therein.**

**Amend claims 1 through 40 as follows:**

1. (Amended) A polyvinyl chloride composition containing an impact [Impact] additive of the core/shell type composed of a core based on alkyl acrylate or on a polyorganosiloxane rubber and a shell based on poly(alkyl methacrylate), or on a styrene-acrylonitrile copolymer, characterized in that the said impact additive comprises from:
  - a) 70 % to 90 % by weight of a crosslinked elastomeric core which is composed;
    - 1) of 20 % to less than 100 % by weight[, and preferably of 20 % to 90 %,] of a nucleus composed of a copolymer (I) of n-alkyl acrylate, the alkyl group of which has a carbon number ranging from 5 to 12, [or of a mixture of alkyl acrylates, the linear or branched alkyl group of which has a carbon number ranging from 2 to 12, or of a polyorganosiloxane rubber,] of a polyfunctional crosslinking agent possessing unsaturated groups in its molecule,

at least one of which is of  $[\text{CH}_2=\text{C}]$  a vinyl [a.] group and optionally of a polyfunctional grafting agent possessing unsaturated groups in its molecule, at least one of which is an [of  $\text{CH}_2=\text{C}-\text{CH}_2-$ ] allyl [type] group, [the said nucleus containing a molar amount of crosslinking agent and optionally of grafting agent ranging from 0.05 % to 5 %,]

2) of not more than 80 % [to 0 %] by weight, [and preferably of 90 % to 10 %,] of a covering composed of a copolymer (II) of n-alkyl acrylate, the alkyl group of which has a carbon number ranging from 4 to 12, or of a grafting agent possessing [a plurality of unsaturated groups in its molecule, at least one of which is of  $\text{CH}_2=\text{CH}-\text{CH}_2-$ ] allyl [type] groups, the said covering containing a molar amount of grafting agent ranging from 0.05 % to 2.5 %, said grafting agent having only allyl functional groups, all having the same reactivity.

b) 30 % to 10 % by weight of a shell grafted onto the said core composed of a polymer of an alkyl methacrylate, the alkyl group of which has a carbon number ranging from 1 to 4, or alternatively of a statistical copolymer of an alkyl methacrylate, the alkyl group of which has a carbon number ranging from 1 to 4, and of an alkyl acrylate, the alkyl group of which has a carbon number ranging from 1 to 8, containing a molar amount of alkyl acrylate ranging from 5 % to 40 %, or alternatively composed of a styrene-acrylonitrile copolymer.

Claim 2, line 1: replace "Impact additive" with --A composition--.

Claim 3, line 1: replace "Impact additive" with --A composition-- and replace "either of" with --claim 1--;

line 2: delete "Claims 1 and 2".

Claim 4, line 1: replace "Impact additive" with --A composition-- and replace "one of" with --claim 1--;

line 2: delete "Claims 1 to 3".

Claim 5, line 1: replace "Impact additive" with --A composition--.

Claim 6, line 1: replace "Impact additive" with --A composition--.

Claim 7, line 1: replace "Impact additive" with --A composition-- and replace "either of" with --claim 1--;

line 2: delete "Claims 1 and 5".

Claim 8, line 1: replace "Impact additive" with --A composition-- and replace "either of" with --claim 1--;

line 2: delete "Claims 1 and 6".

Claim 9, line 1: replace "Impact additive" with --A composition--.

Claim 10, line 1: replace "Impact additive" with --A composition--.

Claim 11, line 1: replace "Impact additive" with --A composition-- and replace "either of" with --claim 1--;

line 2: delete "Claims 1 and 9".

Claim 12, line 1: replace "Impact additive" with --A composition-- and replace "either of" with --claim 1--;

line 2: delete "Claims 1 and 10".

Claim 13, line 1: replace "Impact additive" with --A composition-- and replace "either of" with --claim 1--;

line 2: delete "Claims 1 to 12".

Claim 14, line 1: replace "Impact additive" with --A composition-- and replace "either of" with --claim 1--;

line 2: delete "Claims 1 to 4 and 10 to 12".

Claim 15, line 1: replace "Impact additive" with --A composition-- and replace "either of" with --claim 1--;

line 2: delete "Claims 1 to 4".

Claim 16, line 1: replace "Impact additive" with --A composition-- and replace "either of" with --claim 1--;

line 2: delete "Claims 1 and 3".

Claim 17, line 1: replace "Impact additive" with --A composition-- and replace "either of" with --claim 1--;

line 2: delete "Claims 1 to 3".

Claim 18, line 1: replace "Impact additive" with --A composition-- and replace "Claims 16" with --claim 16--;

line 2: delete "and 17".

Claim 19, line 1: replace "Impact additive" with --A composition-- and replace "Claims 16" with --claim 16--.

line 2: delete "and 17".

Claim 20, line 1: replace "Impact additive" with --A composition-- and replace "Claims 16" with --claim 16--;  
line 2: delete "and 17".

Claim 21, line 1: replace "Impact additive" with --A composition-- and replace "Claims 16" with --claim 16--;  
line 2: delete "and 17".

Claim 22, line 1: replace "Impact additive" with --A composition-- and replace "Claims 16" with --claim 16--;  
line 2: delete "and 17".

Claim 23, line 1: replace "Impact additive" with --A composition-- and replace "one of" with --claim 1--;  
line 2: delete "Claims 1 to 3".

Claim 24, line 1: replace "Impact additive" with --A composition--.

Claim 25, line 1: replace "Impact additive" with --A composition--.

Claim 26, line 1: replace "Impact additive" with --A composition-- and replace "one of" with --claim 23--;  
line 2: delete "Claims 23 to 25".

Claim 27, line 1: replace "Impact additive" with --A composition-- and delete "or";  
line 2: delete "2".

28. (Amended) A thermoplastic [Thermoplastic] polymer composition containing impact additive of the core/shell type composed of a core based on alkyl acrylate or on a polyorganosiloxane rubber and a shell based on poly(alkyl methacrylate), or on a styrene-acrylonitrile copolymer, characterized in that the said impact additive comprises from:

a) 70 % to 90 % by weight of a crosslinked elastomeric core which is composed  
1) of 20 % to less than 100 % by weight of a nucleus composed of a copolymer (I) of n-alkyl acrylate, the alkyl group of which has a carbon number ranging from 5 to 12, of a polyfunctional crosslinking agent possessing unsaturated groups in its molecule, at least one of which is of a vinyl group, and optionally of a polyfunctional grafting agent possessing unsaturated groups in its molecule, at least one of which is an allyl group.

2) of not more than 80 % [to 0 %] by weight, of a covering composed of a copolymer (II) of n-alkyl acrylate, the alkyl group of which has a carbon number ranging from 4 to 12, or of a grafting agent possessing allyl groups, the said covering containing a molar amount of grafting agent ranging from 0.05 % to 2.5 %, said grafting agent having only allyl functional groups, all having the same reactivity,

b) 30 % to 10 % by weight of a shell grafted onto the said core composed of a polymer of an alkyl methacrylate, the alkyl group of which has a carbon number ranging from 1 to 4, or alternatively of a statistical copolymer of an alkyl methacrylate, the alkyl group of which has a carbon number ranging from 1 to 4, and of an alkyl acrylate, the alkyl group of which has a carbon number ranging from 1 to 8, containing a molar amount of alkyl acrylate ranging from 5 % to 40 %, or alternatively composed of a styrene-acrylonitrile copolymer [according to any one of Claims 1 to 27].

29. (Amended) A composition [Composition] according to Claim 28, characterized in that the thermoplastic polymer is composed of at least one polycondensate selected from the group consisting of [one or a number of polymers of the polycondensates type, in particular] polyesters, [such as poly](butylene terephthalate), polyamides, polyesteretheramides, polycarbonates and mixtures thereof [alloys of the abovementioned polymers]

30. (Amended) A composition [Composition] according to Claim 28, characterized in that the thermoplastic polymer is composed of one or a number of polymers selected [chosen] from the group consisting of [formed by] poly(alkyl methacrylate)s, [and in] particular poly(methyl methacrylate) optionally superchlorinated vinyl chloride homopolymers, [;] the copolymers which results from the copolymerization of vinyl chloride with at least one [one or a number of] ethylenically unsaturated comonomers and which contain at least 80 % by weight of polymerized vinyl chloride; 1,1-dichloro-ethylene homopolymer; and [or] 1,1-difluoroethylene homopolymer.

Claim 31, line 1: replace "Composition" with --A composition--.

Claim 32, line 1: replace "Composition" with --A composition--.

Claim 33, line 1: replace "Composition" with --A composition-- and replace "one of Claims" with --claim 28--; and  
line 2: delete "28 to 32".

Claim 34, line 1: replace "Composition" with --A composition--.

Claim 36, line 1: replace "Composition" with --A composition--.

Claim 37, line 1: replace "impact additive" with --composition--.

Claim 38, line 1: replace "impact additive" with --composition--.

Claim 39, line 1: replace "impact additive" with --composition--.

Claim 40, line 1: replace "An impact additive" with --A composition--.

**Add claims 41 through 46 as follows:**

-- 41. A composition according to claim 28, wherein said impact additive comprises:

- 70-90 % by weight of a cross linked elastomeric core compound of:
  - 20-90 % by weight of a nucleus comprising a copolymer of n-octyl acrylate and 1,4-butanediol diacrylate, and
  - surrounding said nucleus, not more than 80% by weight of a covering comprising a copolymer of n-octyl acrylate and diallyl maleate, and
- surrounding said core, 30-10 % by weight of a shell grafted onto the said core, said shell composed of a polymer of an alkyl methacrylate, the alkyl group of which has a carbon number ranging from 1 to 4, or alternatively of a statistical copolymer of an alkyl methacrylate, the alkyl group of which has a carbon number ranging from 1 to 4, and of an alkyl acrylate, the alkyl group of which has a carbon number ranging from 1 to 8, containing a molar amount of alkyl acrylate ranging from 5 % to 40 %, or alternatively composed of a styrene-acrylonitrile copolymer.

42. A composition according to claim 41, wherein said nucleus is about 90 % by weight of said core and, said covering is about 10 % by weight.

43. A composition according to claim 42, wherein said shell consists essentially of poly(methyl methacrylate).

44. An impact resistance additive according to claim 41, wherein said impact additive comprises from:

- a) 75 % to 85 % of said crosslinked elastomeric core,
- b) 25 % to 15 % of said shell grafted onto the said core.

45. A composition according to claim 41, or characterized in that the alkyl methacrylate used to form the shell is methyl methacrylate.

46. A composition according to claim 41, wherein the covering of the crosslinked core has a molar amount of grafting agent of between 0.5 % and 1.5 %. --

#### REMARKS

By virtue of this Preliminary Amendment, there are now forty-six claims which are in three (3) groups:

The first group is directed to a polyvinyl chloride composition to which claims 1-27 and 37-40 are directed.

The second group is claims 28-34 directed to a thermoplastic polymer composition wherein the impact additive is the same as allowed claim 1 of Applicants' parent application.

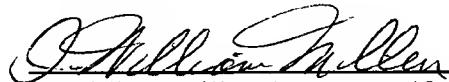
The third group constitutes claims 41-46, directed to a thermoplastic composition wherein the impact additive is the same as allowed claim 41 of Applicants' parent application.

Inasmuch as the second and third groups are based on impact additives which are allowed in the parent application, these groups should be allowed without any rejections predicated on 35 USC §§ 102 or 103.

As for the first group which is directed to a polyvinyl chloride composition, it is to be noted that the reference cited in Applicants' parent application (Aoyama et al.) USP 5,360,865, is directed to a polycarbonate composition. Inasmuch as polyvinyl chloride and a polycarbonate are distinctly different compositions, it is respectfully submitted that one of

ordinary skill in the art having knowledge of an impact additive useful in a polycarbonate composition would not find it obvious to employ the same impact additive in a polyvinyl chloride composition.

Respectfully submitted,



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Filed: June 2, 1998

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IMPACT ADDITIVE OF THE CORE/SHELL TYPE  
FOR THERMOPLASTIC POLYMERS.

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The invention relates to an impact additive.

5 of the core/shell type as well as to a composition containing a thermoplastic polymer, in particular a vinyl chloride homopolymer or a copolymer mostly containing vinyl chloride, an impact additive of the core/shell type and optionally other additives.

10 Some synthetic resins, in particular resins based on poly(vinyl chloride) or on a copolymer mostly containing vinyl chloride, are widely used in the building industry, in particular due to their low cost and to their good physical and/or chemical properties.

15 Nevertheless, they exhibit low impact strengths at ambient temperature or at low temperature or again also after ageing.

It has been proposed to overcome these defects by incorporating, in these thermoplastic 20 resins, products known as impact additives which are generally polymers exhibiting a degree of elastomeric nature.

A description is given in Patent US 3,678,133 of an impact additive of the core/shell type composed 25 of an elastomeric core and of a more rigid thermoplastic shell.

The elastomeric core is obtained by

polymerization of a mixture of monomers comprising at least 50 % by weight of an alkyl acrylate, the alkyl group of which has from 2 to 8 carbon atoms, and a minor proportion of a crosslinking agent. The preferred alkyl acrylate is n-butyl acrylate.

It is also mentioned that alkyl acrylates having longer chains exhibit the disadvantage of polymerizing with greater difficulty. 2-Ethylhexyl acrylate has also been given as an example.

The rigid thermoplastic shell is obtained by polymerization of a mixture of monomers comprising 40 % to 100 % by weight of alkyl methacrylate in which the alkyl group contains 1 to 4 carbon atoms.

The impact additive in this patent is produced in such a way that the polymerization of the rigid thermoplastic shell takes place at the surface of the elastomeric phase, preferably as a separate layer which more or less completely covers the elastomeric core.

Although the impact additives thus obtained significantly improve the impact strength at ambient temperature of the resins containing them, it is however found that there is a loss in the mechanical properties, in particular a loss in the impact strength, at low temperature, of the said resins.

An impact additive of the core/shell type has now been found which is composed of a core based on alkyl acrylate or on a polyorganosiloxane rubber and a

shell based on poly(alkyl methacrylate), or on a styrene-acrylonitrile copolymer, characterized in that the said impact additive comprises from:

a) 70 % to 90 % by weight, and preferably

5 75 % to 85 %, of an elastomeric crosslinked core which  
is composed:

1) of 20 % to 100 % by weight, and

preferably of 20 % to 90 %, of a nucleus composed of a copolymer (I) of n-alkyl acrylate, the alkyl group of

10 which has a carbon number ranging from 5 to 12, and

preferably ranging from 5 to 8, or of a mixture of alkyl acrylates, the linear or branched alkyl group of which has a carbon number ranging from 2 to 12, and preferably ranging from 4 to 8, or of a

15 polyorganosiloxane rubber, of a polyfunctional

crosslinking agent possessing unsaturated groups in its molecule, at least one of which is of  $\text{CH}_2=\text{C}$  vinyl type, and optionally of a polyfunctional grafting agent

20 possessing unsaturated groups in its molecule, at least one of which is of  $\text{CH}_2=\text{CH-CH}_2$ - allyl type, the said nucleus containing a molar amount of crosslinking agent and optionally of grafting agent ranging from 0.05 % to 5 % and preferably an amount of between 0.5 % and 1.5 %:

25. 2) of 80 % to 0 % by weight, and  
preferably of 80 % to 10 %, of a covering composed of a  
copolymer (III) of n-alkyl acrylate, the alkyl group of  
which has a carbon number ranging from 4 to 12, and

preferably ranging from 4 to 8, or of a mixture of alkyl acrylates as defined above in 1) and of a polyfunctional grafting agent possessing unsaturated groups in its molecule, at least one of which is of

5       $\text{CH}_2=\text{CH}-\text{CH}_2-$  allyl type, the said covering containing a molar amount of grafting agent ranging from 0.05 % to 2.5 % and preferably an amount of between 0.5 % and 1.5 %;

10      b) 30 % to 10 % by weight, and preferably 25 % to 15 %, of a shell grafted onto the said core composed of a polymer of an alkyl methacrylate, the alkyl group of which has a carbon number ranging from 1 to 4, or alternatively of a statistical copolymer of an alkyl methacrylate, the alkyl group of which has a

15      carbon number ranging from 1 to 4, and of an alkyl acrylate, the alkyl group of which has a carbon number ranging from 1 to 8, containing a molar amount of alkyl acrylate ranging from 5 % to 40 %, and preferably of between 10 % and 20 %, or alternatively composed of a

20      styrene-acrylonitrile copolymer having a preferred styrene:acrylonitrile molar ratio between 1:1 and 4:1, and particularly between 7:3 and 3:1, respectively.

Mention will be made, as illustration of n-alkyl acrylates which can be used according to the

25      present invention to form the copolymer (I), of n-pentyl acrylate, n-hexyl acrylate, n-heptyl acrylate and very particularly n-octyl acrylate.

Mention will be made, as illustration of n-alkyl acrylates which can be used according to the

30      present invention to form the copolymer (II), of

n-butyl acrylate, n-pentyl acrylate, n-hexyl acrylate, n-heptyl acrylate and very particularly n-octyl acrylate.

The n-alkyl acrylate which may be used to form the copolymers (I) and/or (II) can be identical or different.

Mention will be made, as illustration of linear or branched alkyl acrylates which can be used according to the present invention for the formation of the mixtures of alkyl acrylates constituting the copolymers (I) and/or (II), of ethyl acrylate, n-propyl acrylate, n-butyl acrylate, amyl acrylate, 2-methylbutyl acrylate, 2-ethylhexyl acrylate, n-hexyl acrylate, n-octyl acrylate, n-decyl acrylate, n-dodecyl acrylate or 3,5,5-trimethylhexyl acrylate.

In the case where a mixture of alkyl acrylates is used to produce the copolymers (I) and/or (II), use will be made of an amount by weight of n-alkyl acrylate at least equal to 10 % by weight of the mixture of alkyl acrylates and preferably an amount of between 20 % and 80 %.

As above, use may be made, to form the copolymers (I) and/or (II), of a mixture of identical or different alkyl acrylates.

According to the present invention, it is preferable to use n-alkyl acrylates and very particularly n-octyl acrylate to form the copolymers (I) and (II).

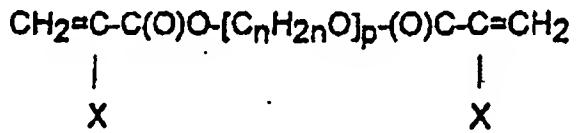
If a mixture of alkyl acrylates is used to form the copolymers (I) and/or (II), use will preferably be made of 20 % to 80 % by weight of n-octyl acrylate and preferably of 80 % to 20 % by weight of 5 n-butyl acrylate.

Mention will be made, as illustration of alkyl methacrylates which can be used to form the shell grafted onto the crosslinked elastomeric core according to the present invention, of ethyl methacrylate, 10 n-propyl methacrylate, isopropyl methacrylate, n-butyl methacrylate, isobutyl methacrylate and very particularly methyl methacrylate.

According to the present invention, the crosslinking agent used to form the copolymer (I) can 15 in particular be chosen from derivatives possessing at least two double bonds of vinyl type or alternatively possessing one or a number of double bonds of vinyl type and at least one double bond of allyl type. Use will preferably be made of compounds possessing, in 20 their molecules, a majority of double bonds of vinyl type.

Mention will be made, as illustration of such crosslinking agents, of divinylbenzenes, polyalcohol (meth)acrylates, such as trimethylolpropane triacrylate, 25 trimethacrylate, allyl acrylate or methacrylate, alkylene glycol diacrylates or dimethacrylates having 2 to 10 carbon atoms in the alkylene chain and in particular ethylene glycol diacrylate or

dimethacrylate, 1,4-butanediol diacrylate or  
dimethacrylate or 1,6-hexanediol diacrylate or  
dimethacrylate, or polyoxyalkylene glycol diacrylate or  
dimethacrylate of formula



5 in which X represents a hydrogen atom or the methyl radical, n is an integer ranging from 2 to 4 and p is an integer ranging from 2 to 20 and in particular polyoxyethylene glycol diacrylate or dimethacrylate in which the polyoxyethylene radical has a molecular mass  
10 of approximately 400 (abovementioned formula with n=2 and p=9).

According to the present invention, the grafting agent used to form the copolymer (II) can be in particular chosen from derivatives possessing at least two double bonds of allyl type or alternatively possessing one or a number of double bonds of allyl type and at least one double bond of vinyl type.

Use will preferably be made of compounds possessing, in their molecules, a majority of double bonds of allyl type.

Mention will be made, as illustration of such grafting agents, of diallyl maleate, diallyl itaconate, allyl methacrylate or acrylate, triallyl cyanurate, triallyl isocyanurate, diallyl terephthalate or

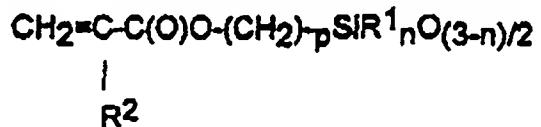
triallyl trimesate.

According to an alternative form in accordance with the invention, the nucleus of the crosslinked elastomeric core can be composed entirely 5 of a polyorganosiloxane rubber obtained by emulsion polymerization of an organosiloxane in the presence of a crosslinking agent and, optionally, of a grafting agent.

Mention may be made, as illustration of 10 organosiloxanes, of cyclic siloxanes composed of rings having a number of Si-C ring members ranging from 3 to 6, such as hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane, dodecamethylcyclohexasiloxane or 15 octaphenylcyclotetrasiloxane.

Mention may be made, as crosslinking agent which can be used, of a crosslinking agent of the tri- or tetrafunctional silane type, such as, for example, trimethoxysilane or tetraethoxysilane.

20 Use will preferably be made, as grafting agent, of a methacryloyloxy siloxane of formula:



in which  $\text{R}^1$  represents a methyl, ethyl, propyl or phenyl group,  $\text{R}^2$  represents a hydrogen atom or a methyl group,  $n$  has a value 0, 1 or 2 and  $p$  is a

number ranging from 1 to 6.

Mention may be made, as illustration of methacryloyloxy siloxane, of:

### $\beta$ -methacryloyloxyethyl dimethoxymethylsilane,

$\gamma$ -methacryloyloxypropylmethoxydimethylsilane,

*γ*-methacryloyloxypropylmethoxysilane.

### $\gamma$ -methacryloxypropyltrimethoxysilane.

$\gamma$ -methacryloyloxypropylethoxydiethylsilane,

### $\gamma$ -methacryloyloxypropyl diethoxymethylsilane

10 and

### **$\delta$ -methacryloyloxybutyldiethoxymethylsilane.**

The polyorganosiloxane rubber can be produced by a process described, for example, in European Patent EP 0,326,038. Use will very particularly be made of the procedure described in the example of reference 1 of the said patent, which makes it possible to obtain a polyoctamethylcyclotetrasiloxane rubber latex.

According to this alternative form, the crosslinked elastomeric core can contain no more than 40 % by weight of a nucleus composed of a polyorganosiloxane rubber as described above.

The invention also relates to a composition comprising a thermoplastic polymer and the impact additive as defined above.

25 The thermoplastic polymer can be composed of  
one or a number of polymers of the polycondensates  
type, in particular polyamides, polyetheresteramides  
(PEBAX), polyesters, such as polybutylene

terephthalate, polycarbonates or alloys of the abovementioned polymers, such as alloys of polycarbonates and of polyesters, such as XENOY. The thermoplastic polymer can also be composed of one or a 5 number of polymers chosen from the group formed by poly(alkyl methacrylate)s and in particular poly(methyl methacrylate) or by vinyl chloride homopolymers, which can optionally be superchlorinated, and copolymers which result from the copolymerization of vinyl 10 chloride with one or a number of ethylenically unsaturated comonomers and which contain at least 80 % by weight of polymerized vinyl chloride. Examples of monomers which are suitable for the preparation of such copolymers are in particular vinylidene halides, such 15 as vinylidene chloride or fluoride, vinyl carboxylates, such as vinyl acetate, vinyl propionate or vinyl butyrate, acrylic and methacrylic acids and the nitriles, amides and alkyl esters which derive therefrom, in particular acrylonitrile, acrylamide, 20 methacrylamide; methyl methacrylate, methyl acrylate, butyl acrylate, ethyl acrylate or 2-ethylhexyl acrylate, vinylaromatic derivatives, such as styrene or vinylnaphthalene, or olefins, such as bicyclo[2.2.1]hept-2-ene, bicyclo[2.2.1]hepta-2,5- 25 diene, ethylene, propene or 1-butene.

The thermoplastic polymer can also be composed of a homopolymer of a vinylidene halide, such as 1,1-dichloroethylene or 1,1-difluoroethylene.

The thermoplastic polymer is preferably a vinyl chloride homopolymer or a poly(butylene terephthalate).

The preferred content of impact additive 5 incorporated in the thermoplastic polymer is between 1 and 30 parts by weight, and preferably between 5 and 10 parts by weight, per 100 parts by weight of the thermoplastic polymer used.

In order to describe the molecular mass of 10 the impact additive, it is possible to define a viscosity in the molten state which varies in the same sense. The said viscosity in the molten state may be situated in a fairly wide range, provided that the impact additive is well dispersed during the operations 15 in which the resin composition, including the said additive, is made use of. As representative magnitude of this viscosity in the molten state, the value of the resisting torque of a Brabender rheometer containing 50 g of impact additive and operating at a temperature of 20 200°C with a rotational speed of its rotors equal to 40 revolutions per minute may suitably be taken, the torque being determined after holding at 200°C for 20 minutes. Appropriate values of the viscosity in the molten state for the impact additive correspond to 25 values of the abovementioned torque of between 600 and 4000 m.g. In the case of resin compositions for which the thermoplastic polymer is a polymer containing at least 80 % by weight of polymerized vinyl chloride,

preferred viscosity values in the molten state for the impact additive correspond to values of the said torque ranging from 800 to 3000 m.g. and very particularly from 1000 to 2500 m.g.

5 Another subject of the invention is a process for producing the said impact additive.

One process comprises the preparation, in a first stage, of a crosslinked core composed of a nucleus and of a covering and then, in a second stage, 10 a poly(alkyl methacrylate) shell is grafted onto the said crosslinked core obtained in the first stage.

According to a preferred method, the crosslinked core, composed of a nucleus and of a covering, is prepared and the grafting operation is 15 carried out by using emulsion polymerization techniques. In this case, the following procedure can be used.

In a first stage, an emulsion is prepared which contains, per part by weight of monomers to be polymerized, 1 to 10 parts of water, 0.001 to 20 0.03 parts of an emulsifying agent, a major portion of the n-alkyl acrylate or of the mixture of alkyl acrylates as defined above to be polymerized in order to form the said core and at least one polyfunctional crosslinking agent. The reaction mixture thus formed is 25 stirred and maintained at a temperature ranging from 55°C to 65°C and preferably at a temperature in the region of 60°C. 0.001 to 0.5 parts of a catalyst which generates free radicals is then added and the reaction

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mixture thus formed is maintained at a temperature of, for example, between ambient temperature and 100°C and with stirring for a period sufficient to obtain a virtually complete conversion of the monomers. The 5 minor portion of n-alkyl acrylate or of the mixture of alkyl acrylates and the grafting agent, as well as, at the same time, 0.001 to 0.005 part of a catalyst which generates free radicals, are then added simultaneously to the phase thus obtained.

10 This second operation of the first stage, which comprises the production of the covering, is generally carried out at a temperature greater than that used for the preparation of the nucleus. This temperature is not greater than 100°C and preferably 15 between 60°C and 90°C.

An alternative form of this first stage comprises the production of the crosslinked core in a single operation by simultaneously introducing the crosslinking agent and the grafting agent (or a 20 compound which plays both the crosslinking role and the grafting role) into the reaction mixture.

In a second stage, the said core is grafted with an alkyl methacrylate. To do this, an appropriate amount of the said methacrylate is added to the 25 reaction mixture resulting from the first stage, in order to obtain a grafted copolymer containing the desired content of grafted chains, as well as, if appropriate, additional amounts of emulsifying agent

and of a radical catalyst also within the ranges defined above, and the mixture thus formed is maintained at a temperature within the abovementioned range, with stirring, until virtually complete 5 conversion of the grafting monomers is obtained.

Use may be made, as emulsifying agent, of any one of the known surface-active agents, whether anionic, nonionic or even cationic. In particular, the emulsifying agent may be chosen from anionic 10 emulsifying agents, such as sodium or potassium salts of fatty acids, in particular sodium laurate, sodium stearate, sodium palmitate, sodium oleate, mixed sulphates of sodium or of potassium and of fatty alcohols, in particular sodium lauryl sulphate, sodium 15 or potassium salts of sulphosuccinic esters, sodium or potassium salts of alkylarylsulphonic acids, in particular sodium dodecylbenzenesulphonate, and sodium or potassium salts of fatty monoglyceride monosulphonates, or alternatively from nonionic 20 surfactants, such as the reaction products of ethylene oxide and of alkylphenol or of aliphatic alcohols, alkylphenols. Use may also be made of mixtures of such surface-active agents, if need be.

The catalysts capable of being employed, both 25 in the abovementioned first emulsion polymerization stage and in the abovementioned second emulsion polymerization stage, are compounds which give rise to free radicals under the temperature conditions chosen

for the polymerization. These compounds can in particular be peroxide compounds, such as hydrogen peroxide; alkali metal persulphates and in particular sodium or potassium persulphate; ammonium persulphate, 5 percarbonates; paracetates, perborates; peroxides such as benzoyl peroxide or lauroyl peroxide; or hydroperoxides such as cumene hydroperoxide, diisopropylbenzene hydroperoxide, para-menthane hydroperoxide or tert-butyl hydroperoxide.

10 However, it is preferable to use catalytic systems of redox type formed by the combination of a peroxide compound, for example as mentioned above, with a reducing agent, in particular such as alkali metal sulphite, alkali metal bisulphite; sodium formaldehyde 15 sulphoxylate ( $\text{NaHSO}_2 \cdot \text{HCHO}$ ), ascorbic acid, glucose, and in particular those of the said catalytic systems which are water-soluble, for example potassium persulphate/sodium metabisulphite or alternatively diisopropylbenzene hydroperoxide/sodium formaldehyde sulphoxylate.

20 It is also possible to add, to the polymerization mixture of one and/or other of the stages, chain-limiting compounds, and in particular mercaptans such as tert-dodecyl mercaptan, isobutyl mercaptan, n-octyl mercaptan, n-dodecyl mercaptan or isooctyl mercaptopropionate, for the purpose of 25 controlling the molecular mass of the core and/or of the chains grafted onto the nucleus, or alternatively

compounds such as phosphates, for the purpose of controlling the ionic strength of the polymerization mixture.

The reaction mixture obtained on conclusion 5 of the second emulsion polymerization stage, which is composed of an aqueous emulsion of the additive according to the invention, is then treated in order to separate the said additive therefrom. To do this, it is possible, for example, to subject the emulsion, 10 according to the surfactant used, to a coagulating treatment by bringing into contact with a saline solution ( $\text{CaCl}_2$  or  $\text{AlCl}_3$ ) or a solution acidified with concentrated sulphuric acid and then to separate, by filtration, the solid product resulting from the 15 coagulating, the said solid product then being washed and dried to give a graft copolymer as a powder. It is also possible to recover the additive contained in the emulsion by using a spray-drying technique.

The resulting additive exists in the form of 20 a powder, the particle size of which can range from a few microns, for example 0.05 to 5 microns, to 200 to 300 microns, the said particle size depending on the technique used to separate the graft copolymer from the emulsion polymerization mixture.

25 The composition according to the invention can be prepared by any method which makes it possible to produce a homogeneous mixture containing a thermoplastic polymer, the impact additive according to

the invention and optionally other additives. It is possible, for example, to dry-mix the ingredients constituting the resin composition, then to extrude the resulting mixture and to reduce the extrudate to 5 pellets. When the thermoplastic polymer is obtained by emulsion polymerization, it may be convenient to mix the emulsion containing the additive according to the invention with the emulsion of the thermoplastic polymer and to treat the resulting emulsion in order to 10 separate therefrom the solid product which it contains, as described above with respect to the separation of the additive.

The additives, other than the impact additive, which may optionally be present in the resin compositions according to the invention are in particular those such as pigments, dyes, plasticizers, antioxidants, heat stabilizers, processing additives or lubricants.

20 The PVC composition obtained according to the present invention exhibits excellent impact strength at ambient temperature as well as at temperatures as low as -30°C or even -40°C.

The composition of the present invention can advantageously be used to produce sections or claddings 25 used in particular in the building industry or alternatively to produce pipes which can be used for conveying water.

The following examples illustrate the

invention.

Example 1 (according to the invention)

The preparation is carried out in a 2-litre reactor equipped with a stirrer device and a temperature recorder and provided with a jacket through which passes a heat-transfer fluid for maintaining the temperature of the reactor.

5 1) Preparation of the crosslinked elastomeric core of the impact additive:

10 800 g of demineralized water and 2.46 g of disodium phosphate are introduced, after having degassed with nitrogen, into the reactor described above, maintained at ambient temperature and with stirring, and then 20.58 g of sodium lauryl sulphate 15 are dissolved in this mixture as emulsifying agent.

The temperature of the contents of the reactor is then brought to 57°C and 423 g of n-octyl acrylate and 5.08 g of 1,4-butanediol diacrylate are then added simultaneously to the said contents, while 20 maintaining this temperature.

The temperature of the reactor is brought to 63°C and 0.41 g of sodium metabisulphite in 5.59 ml of water and 0.62 g of potassium persulphate in 6.58 ml of water are then added to the reaction mixture as 25 catalytic system. The reaction is then allowed to continue for 2 hours, the temperature of the reactor is then brought to 80°C and 47 g of n-octyl acrylate, 2.36 g of diallyl maleate and 0.8 g of potassium

persulphate are then added simultaneously.

The temperature of the reactor is maintained at 80°C for 1 hour. A crosslinked elastomeric core is obtained, with a conversion of 98 %, consisting of:

5 1) 89.66 % by weight of a nucleus composed of an n-octyl acrylate/1,4-butanediol diacrylate copolymer (I) and of

2) 10.34 % by weight of a covering composed of an n-octyl acrylate/diallyl maleate copolymer (II).

10 This core contains, in moles, 1 % of 1,4-butanediol diacrylate and 0.47 % of diallyl maleate.

2) Grafting of the methyl methacrylate onto the crosslinked elastomeric core:

15 118 g of methyl methacrylate are continuously added over one hour, with stirring, to the reaction mixture obtained above maintained at 80°C. 1.7 g of diisopropylbenzene hydroperoxide in 78 ml of water and 0.2 g of sodium formaldehyde sulphoxylate in 4 ml of water are also added at the same time.

20 The contents of the reactor are maintained at 80°C for 1.5 hours, after the beginning of the introduction of the methyl methacrylate, and 0.31 g of tert-butyl hydroperoxide and 0.8 g of sodium metabisulphite in 15 ml of water are added to the said 25 contents. The reaction mixture is then maintained at 80° for one hour. At the end of this period, the contents of the reactor are cooled to ambient temperature and the grafted copolymer latex produced.

the mean particle diameter of which is 0.08  $\mu\text{m}$ . is coagulated in a saline solution acidified with concentrated sulphuric acid. The coagulated product is then filtered, washed and then dried to give a powder 5 constituting the impact additive.

The conversion of the methyl methacrylate during the grafting is 99 %. The impact additive contains a proportion of grafted poly(methyl methacrylate) chains representing 19.82 % by weight of 10 the additive and has a viscosity in the molten state corresponding to a value equal to 1400 m.g. of the torque of the Brabender rheometer operating under the conditions defined above.

Example 2 (in accordance with the invention)

15 1) Preparation of the crosslinked elastomeric core of the impact additive:

2000 g of demineralized water and 5.85 g of disodium phosphate are introduced, after having degassed with nitrogen, into a 5-litre reactor equipped 20 as described in Example 1 maintained at room temperature and with stirring and then 245 g of sodium lauryl sulphate are dissolved in this mixture as emulsifying agent.

The temperature of the contents of the 25 reactor are then brought to 57°C and 904.5 g of n-octyl acrylate, 301.5 g of n-butyl acrylate and 14.4 g of 1,4-butanediol diacrylate are then simultaneously added to the said contents, while maintaining this

temperature.

The temperature of the reactor is brought to 63°C and 22.6 g of sodium bisulphite in 10 ml of water and 1.60 g of potassium persulphate in 33.83 ml of water are then added to the reaction mixture as catalytic system. The reaction is then allowed to continue under adiabatic conditions for 2 hours, the temperature of the reactor is then brought to 80°C and 100.5 g of n-octyl acrylate, 33.5 g of n-butyl acrylate, 6.71 g of diallyl maleate and 0.17 g of potassium persulphate in 3.73 ml of water are then added simultaneously.

The temperature of the reactor is maintained at 80°C for 1 hour.

15 A crosslinked elastomeric core is obtained, with a conversion of 95.72 %, consisting of:

1) 89.66 % by weight of a nucleus composed of an n-octyl acrylate/n-butyl acrylate/1,4-butanediol diacrylate copolymer (I) and of

20 2) 10.34 % by weight of a covering composed of an n-octyl acrylate/n-butyl acrylate/dialkyl maleate copolymer (II).

2) Grafting of the methyl methacrylate onto the crosslinked elastomeric core:

25 335.3 g of methyl methacrylate are continuously added over one hour, with stirring, to the reaction mixture obtained above maintained at 80°C. 4.3 g of diisopropylbenzene hydroperoxide in 195.7 ml

of water and 0.40 g of sodium formaldehyde sulphoxylate in 9.28 ml of water are also added at the same time.

The contents of the reactor are maintained at 80°C for 1.5 hours, after the beginning of the 5 introduction of the methyl methacrylate, and 0.24 g of tert-butyl hydroperoxide and 4.6 g of sodium bisulphite in 17 ml of water are added to the said contents. The reaction mixture is then maintained at 80° for one hour. At the end of this period, the contents of the 10 reactor are cooled to ambient temperature and the grafted copolymer latex produced is coagulated in a saline solution acidified with concentrated sulphuric acid. The coagulated product is then filtered, washed and then dried to give a powder constituting the impact 15 additive.

The conversion of the methyl methacrylate during the grafting is 98.27 %. The impact additive contains a proportion of grafted poly(methyl methacrylate) chains representing 19.77 % by weight of 20 the additive and has a viscosity in the molten state corresponding to a value equal to 1500 m.g. of the torque of the Brabender rheometer operating under the conditions defined above.

In Examples 3 to 7, the preparation is 25 carried out according to the same operating conditions of Example 1, using, for the crosslinked elastomeric core as for the shell grafted onto the said core, the same reactants (grafting and crosslinking agents,

catalysts, emulsifiers, and the like) in identical amounts by weight, except that, for the preparation of the crosslinked elastomeric core, use is made of identical amounts by weight of an alkyl acrylate other than n-octyl acrylate, to produce the copolymers (I) and (II).

In Example 3, n-heptyl acrylate is used.

In Example 4, n-hexyl acrylate is used.

In Example 5, n-pentyl acrylate is used.

10 In Example 6 (not in accordance with the invention), n-butyl acrylate is used.

In Example 7 (not in accordance with the invention), 2-ethylhexyl acrylate is used.

Impact additives are obtained which contain, 15 as in Example 1, a crosslinked elastomeric core, obtained with yields greater than 98 %, consisting of:

1) approximately 90 % by weight of a nucleus composed of an alkyl acrylate/1,4-butanediol diacrylate copolymer (I) and of

20 2) approximately 10 % by weight of a covering composed of an alkyl acrylate copolymer (II) identical to that used in 1/dialkyl maleate, and a shell, made of poly(methyl methacrylate), grafted onto the said core and representing approximately 20 % 25. by weight of the impact additive. ----

Example 8 (in accordance with the invention)

1) Preparation of the crosslinked elastomeric core of the impact additive:

750 g of demineralized water, 2.46 g of disodium phosphate and 0.41 g of sodium metabisulphite in 7.59 ml of water are introduced, after having degassed with nitrogen, into the reactor described in 5 Example 1, maintained at ambient temperature and with stirring, and then 100 g of sodium lauryl sulphate are dissolved in this mixture as emulsifying agent.

The temperature of the contents of the reactor is then brought to 57°C and 117.5 g of n-octyl 10 acrylate and 1.21 g of allyl methacrylate are then added simultaneously to the said contents, while maintaining this temperature.

The temperature of the reactor is brought to 63°C and 0.13 g of potassium persulphate in 2.67 ml of 15 water is then added to the reaction mixture. The reaction is then allowed to continue for 45 minutes, the temperature of the reactor is then brought to 80°C and 353 g of n-butyl acrylate, 5.21 g of allyl methacrylate and 0.5 g of potassium persulphate in 20 10.7 ml of water are then added simultaneously.

The temperature of the reactor is maintained at 80°C for 1 hour.

A crosslinked elastomeric core is obtained, with a conversion of 99.9 %, consisting of

25 1) 24.89 % by weight of a nucleus composed of an n-octyl acrylate/allyl methacrylate copolymer (I) and of

2) 75.11 % by weight of a covering composed

of an n-butyl acrylate/allyl methacrylate copolymer (II).

2) Grafting of the methyl methacrylate onto the crosslinked elastomeric core:

5        118 g of methyl methacrylate are continuously added over one hour, with stirring, to the reaction mixture obtained above maintained at 80°C. 1.7 g of diisopropylbenzene hydroperoxide in 78 ml of water and 0.42 g of sodium formaldehyde sulphoxylate in 9.58 ml 10 of water are also added at the same time.

The contents of the reactor are maintained at 80°C for 1.5 hours, after the beginning of the introduction of the methyl methacrylate, and 0.33 g of tert-butyl hydroperoxide and 0.08 g of sodium 15 metabisulphite in 10 ml of water are added to the said contents. The reaction mixture is then maintained at 80° for one hour. At the end of this period, the contents of the reactor are cooled to ambient temperature and the grafted copolymer latex produced is 20 coagulated in a saline solution acidified with concentrated sulphuric acid. The coagulated product is then filtered, washed and then dried to give a powder constituting the impact additive.

The conversion of the methyl methacrylate 25 during the grafting is quantitative. The impact additive contains a proportion of poly(methyl methacrylate) graft chains representing 19.83 % by weight of the additive and has a viscosity in the

molten state corresponding to a value equal to 1760 m.g. of the torque of the Brabender rheometer operating under the conditions defined above.

Example 9 (in accordance with the invention)

5

The preparation is carried out in a 2-litre reactor equipped with a stirring device and a temperature recorder and provided with a jacket through which passes a heat-transfer fluid for maintaining the temperature of the reactor.

10

1) Preparation of the crosslinked elastomeric core of the impact additive:

15

787.5 g of demineralized water, 2.58 g of disodium phosphate and 0.42 g of sodium metabisulphite in 7.98 ml of water are introduced, after having degassed with nitrogen, into the reactor described above maintained at ambient temperature and with stirring and then 105 g of sodium lauryl sulphate are dissolved in this mixture as emulsifying agent.

20

The temperature of the contents of the reactor are then brought to 57°C and 493.50 g of n-octyl acrylate and 3.38 g of allyl methacrylate are then added simultaneously to the said contents, while maintaining this temperature.

25

The temperature of the reactor is brought to 63°C and 0.66 g of potassium persulphate in 14 ml of water is then added to the reaction mixture. The reaction is then allowed to continue for 2 hours and then the temperature of the reactor is brought to 80°C.

The temperature of the reactor is maintained at 80°C for 1 hour. A crosslinked elastomeric core is obtained, with a conversion of 98.95 %, consisting of an n-octyl acrylate/allyl methacrylate copolymer (I).

5 This core contains, in moles, 1 % of allyl methacrylate.

2) Grafting of methyl methacrylate onto the crosslinked elastomeric core:

118 g of methyl methacrylate are continuously 10 added over one hour, with stirring, to the reaction mixture obtained above maintained at 80°C. 1.7 g of diisopropylbenzene hydroperoxide in 78 ml of water and 0.42 g of sodium formaldehyde sulphoxylate in 9.58 ml of water are also added at the same time.

15 The contents of the reactor are maintained at 80°C for 1.5 hours, after the beginning of the introduction of the methyl methacrylate, and 0.33 g of tert-butyl hydroperoxide and 0.08 g of sodium metabisulphite in 10 ml of water are added to the said 20 contents. The reaction mixture is then maintained at 80° for one hour. At the end of this period, the contents of the reactor are cooled to ambient temperature and the grafted copolymer latex produced is coagulated in a saline solution acidified with 25 concentrated sulphuric acid. The coagulated product is then filtered, washed and then dried to give a powder constituting the impact additive.

The conversion of the methyl methacrylate

during the grafting is 96.17 %. The impact additive contains a proportion of poly(methyl methacrylate) graft chains representing 19.82 % by weight of the additive and has a viscosity in the molten state 5 corresponding to a value equal to 1300 g.m. of the torque of the Brabender rheometer operating under the conditions defined above.

Example 10:

1. Preparation of the crosslinked elastomeric 10 core of the impact additive.

First stage: Preparation of the seed.

The preparation is carried out in a 5-litre reactor equipped with a stirrer, a temperature recorder and a jacket through which passes a heat-transfer fluid 15 for maintaining the temperature of the reactor.

1,100 g of demineralized water and 0.95 g of sodium hydrogencarbonate in 95 g of water are introduced, after having degassed with nitrogen, into this reactor maintained at ambient temperature and with 20 stirring and then 4.76 g of sodium dioctyl sulphosuccinate are dissolved in this mixture as emulsifying agent.

The temperature of the contents of the reactor is then brought to 57°C and, while maintaining 25 this temperature, 119 g of n-octyl acrylate and 2.56 g of 1,4-butanediol diacrylate are then added simultaneously to the said contents.

The temperature of the reactor is brought to

70°C and 2.62 g of potassium persulphate, dissolved in 65 g of water, are added to the reaction mixture.

After an induction time of approximately 10 minutes, the temperature rises to 76°C. An 5 emulsified mixture composed of 663 g of demineralized water, 0.66 g of sodium hydrogencarbonate in 66 g of water, 6.43 g of sodium dioctyl sulphosuccinate as emulsifying agent, 1.071 g of n-octyl acrylate and 23.05 g of 1,4-butanediol diacrylate is then added to 10 the reactor over a period of two hours. The temperature is maintained at 70°C during the addition period. The temperature is then increased to 90°C and maintained for one hour.

A crosslinked elastomeric seed, denoted by 15 "emulsion (A)", is obtained, with a conversion of 99 %, consisting of latex particles with a diameter of 0.130  $\mu\text{m}$ .

Second stage: Preparation of the core.

The preparation is carried out in a 5-litre 20 reactor equipped with a stirrer, a temperature recorder and a jacket through which passes a heat-transfer fluid for maintaining the temperature of the reactor.

An emulsified premix (B) is prepared composed of 660 g of demineralized water, 0.66 g of sodium 25 hydrogencarbonate in 66 g of water, 6.43 g of sodium dioctyl sulphosuccinate as emulsifying agent, 1.071 g of n-octyl acrylate and 23.05 g of 1,4-butanediol diacrylate.

The reactor being maintained at room temperature and with stirring, 1,000 g of demineralized water and 1 g of sodium hydrogencarbonate in 100 g of water are introduced, after having degassed with 5 nitrogen, and then 338.88 g of the emulsion(A) obtained during the first stage are dissolved in this mixture.

The temperature of the contents of the reactor is then brought to 57°C and 120 g of the premix (B) are then added, while maintaining this temperature.

10 The temperature of the reactor is brought to 70°C and 2.14 g of potassium persulphate, dissolved in 65 g of water, are added to the reaction mixture.

After an induction time of approximately 10 minutes, the temperature rises to 76°C. 1,505 g of 15 the premix(B) are then added to the reactor over a period of 110 minutes. 5.95 g of diallyl maleate are then added to the remaining 200 g of premix B and the combined mixture is added to the contents of the reactor, while still maintaining the temperature at 20 70°C, over a period of 10 minutes.

The temperature is then increased to 90°C and maintained for one hour.

The elastomeric core is obtained, with a conversion of 99 %, consisting of latex particles with 25 a Coulter diameter of 0.270  $\mu\text{m}$ .

2. Grafting of methyl methacrylate onto the crosslinked elastomeric core

0.54 g of potassium persulphate, dissolved in 30 g of water, is added, with stirring, to the reaction mixture obtained above maintained at 70°C. An emulsified mixture (C), composed of 200 g of demineralized water, 0.35 g of sodium hydrogencarbonate in 35 g of water, 1.34 g of sodium dioctyl sulphosuccinate as emulsifying agent, 267 g of methyl methacrylate and 29.75 g of ethyl acrylate, is then added continuously over 45 minutes.

On completion of this addition, the contents of the reactor are maintained at 90°C for one hour. At the end of this period, the contents of the reactor are cooled to ambient temperature.

A grafted copolymer latex is obtained, with a conversion of 98.3 %, the mean particle diameter of which is 0.285  $\mu\text{m}$ .

This latex is then coagulated in a calcium chloride solution. The coagulated product is then filtered, washed and then dried to give a powder which constitutes the impact additive.

This additive has a viscosity in the molten state corresponding to a value equal to 890 m.g. of the Brabender rheometer torque operating under the conditions defined above.

Example 11 (not in accordance with the invention)

The preparation is carried out according to the same operating conditions as Example 10, use being 5 made, for the preparation of the seed, of the crosslinked elastomeric core and for the shell grafted onto the said core, of the same reactants (grafting and crosslinking agents, catalysts, emulsifiers, and the like) in identical amounts by weight, except that, for 10 the preparation of the seed and of the crosslinked elastomeric core, use is made of an amount by weight identical of 2-ethylhexyl acrylate in place of n-octylacrylate.

A grafted copolymer latex is obtained, with a 15 conversion of 99.1%, the mean particle diameter of which is 0.315  $\mu\text{m}$ .

This latex is then coagulated in a calcium chloride solution. The coagulated product is then filtered, washed and then dried to give a powder which 20 constitutes the impact additive.

This additive has a viscosity in the molten state corresponding to a value equal to 1,725 m.g. of the Brabender rheometer torque operating under the conditions defined above.

25 Example 12 (not in accordance with the invention)

The preparation is carried out according to the same operating conditions as Example 10, use being

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made, for the preparation of the seed, of the crosslinked elastomeric core and for the shell grafted onto the said core, of the same reactants (grafting and crosslinking agents, catalysts, emulsifiers, and the like) in identical amounts by weight, except that, for the preparation of the seed and of the crosslinked elastomeric core, use is made of an identical amount by weight of butyl acrylate in place of *n*-octyl acrylate and of an identical molar amount, with respect to the butyl acrylate monomer, of 1,4-butanediol diacrylate.

A grafted copolymer latex is obtained, with a conversion of 98.6 %, the mean particle diameter of which is 0.335  $\mu\text{m}$ .

This latex is then coagulated in a calcium chloride solution. The coagulated product is then filtered, washed and then dried to give a powder which constitutes the impact additive.

This additive has a viscosity in the molten state corresponding to a value equal to 1,725 m.g. of the Brabender rheometer torque operating under the conditions defined above.

Preparation and characteristics of the resin compositions according to the invention:

1. The description is given below of the preparation of a PVC-based resin composition and the impact strength characteristics of test specimens manufactured from this resin composition are given.

The preparation is carried out at 25°C, in a

mixer of the Papenmeir type, of a composition containing (parts by weight):

- 100 parts of a vinyl chloride homopolymer of K-value = 67,

5 - 2.5 parts of lead phosphite,

- 1.5 parts of calcium stearate,

- 6 parts of calcium carbonate,

- 4 parts of  $TiO_2$ ,

- 1 part of a processing aid (Metablen P550,

10 sold by the company Metablen B.V.),

- 0.2 part of 12 stearic acid,

- 0.3 part of Loxiol G60 (internal lubricant),

15 - 4 parts of polyethylene waxes (external lubricant) and,

- x parts of an impact additive prepared according to one of Examples 1 to 9.

From the composition thus obtained, test specimens are prepared for carrying out the impact 20 strength determination tests.

To prepare the test specimens for the Charpy impact tests, the PVC resin compositions resulting from the mixtures of the abovementioned ingredients are calandered at 175°C for 6 minutes on a calender of the 25 Schwanbenthal type and then moulded at 190°C on a Derragon press, for 5 minutes under a pressure of 200 bar, in the form of panels, the said panels being cooled in the press.

The test specimens are cut out using a circular saw and then a notcher for the notched Charpy impact tests, according to BS standard 2782.

5 The thickness of the test specimens, the shape of which is that stipulated by the abovementioned standard, is 2.5 mm.

To prepare the test specimens for the low-temperature impact strength test according to ISO standard 6603.2 1989 (F), the resin composition defined 10 above is mixed in a twin-screw extruder of the Krauss-Maffei KMD 25 type, then introduced into a die, which makes it possible to obtain a strip with a thickness of 1 mm, and then cut up into 7 cm x 7 cm squares.

15 The results are combined in the tables below.

In Table 1, the source of the impact additive (example) and its content in the PVC resin composition as described above, in parts by weight per 100 parts by weight of the said resin (phr), have been shown in the "impact additive" column. The "Charpy impact" strength 20 tests are carried out according to BS standard 2782 at a temperature of  $23 \pm 1^\circ\text{C}$ . The fracture energy is calculated by taking the mean of the ductile and brittle fracture energies.

25 The low-temperature impact strength tests are reported in Table 2. As in Table 1, the source of the said impact additive and its content (phr) in the PVC resin composition have been shown in the "impact additive" column.

In Tables 1 and 2, the compositions 9(c), 10(c), 11(c), 12(c), 21(c) and 22(c) are not in accordance with the invention.

2. The preparation of a resin composition

5 based on poly(butylene terephthalate) (PBT) is described below and the impact strength characteristics of test specimens manufactured from this resin composition are given.

10 The preparation is carried out at 25°C of a resin composition according to the invention containing (parts by weight):

- 80 parts of a poly(butylene terephthalate) homopolymer (Calanex 1700A, sold by the company Hoechst Celanese),

15 - 20 parts of an impact additive prepared according to one of Examples 10 to 12.

The mixture is dried for at least 10 hours under a vacuum of 1 bar at 80°C.

20 This mixture is homogenized by extrusion on a Buss PR46 Ko-Kneader, followed by granulation of the rod obtained. The extrusion conditions are as follows:

Ko-Kneader	- temperature of the screw:	230°C
	temperature zone 1:	260°C
	temperature zone 2:	250°C
25	speed:	120 revolutions/minute
Extruder	- temperature of the screw:	240°C
	temperature zone 1:	240°C
	die:	230°C

speed: 94 revolutions/  
minute

The test specimens for the Izod impact tests are prepared by injection moulding the granules obtained above on a Visumat 5000 injection press. These granules are dried for at least 10 hours under a vacuum of 1 bar at 80°C. Injection is carried out under the following conditions:

	Injection temperature:	240°C
10	Injection rate:	10 %
	Injection pressure:	80 bar
	Hold pressure:	50 bar
	Hold time:	20 seconds

These test specimens, the shape and thickness of which are those described in ISO standard 180, are then notched.

The results obtained are presented in the table below. In Table 3, the source of the impact additive (Example) has been shown in the "impact additive" column. The fracture energy according to ISO standard 180 at a temperature of 23 ± 1°C, calculated by taking the mean of the ductile and brittle fractures with respect to ten test specimens, has been reported in the "ambient temperature impact" column. The fracture energy according to ISO standard 180 at a temperature of -20°C ± 1°C, calculated by taking the mean of the ductile and brittle fractures with respect to ten test specimens, has been reported in the "cold impact" column.

3. The preparation of a resin composition based on poly(1,1-difluoroethylene) (PVDF) is described below and the impact strength characteristics of test specimens manufactured from this resin composition 5 are given.

The preparation is carried out at 25°C of a resin composition according to the invention containing (parts by weight) :

- 95 parts of a poly(1,1-difluoroethylene) 10 homopolymer (Kynar 1000, sold by the company ELF ATOCHEM S.A.),

- 5 parts of an impact additive prepared according to Examples 10 and 12.

The mixture is homogenized by extrusion on a Werner 15 40, followed by granulation of the rod obtained. The extrusion conditions are as follows :

- temperature zone 1 : 195°C  
- temperature zone 2 : 230°C  
- temperature zone 3 : 215°C  
20 - temperature zone 4 : 240°C.

The test specimens for the Izod impact and Charpy impact tests are prepared by injection moulding the granules obtained above on a Visumat 5000 injection press in the shape of sheet of 100 mm x 100 mm.

25 These test specimens, the shape and thickness of which are those described in ISO standard 179 and ISO standard, are punched with tool.

The results obtained are presented in the table 4. In this Table 4, the source of the impact additive (Example) has been shown in the "impact additive" column. The fracture energy according to ISO standard 5 180 at a temperature of  $23^{\circ}\text{C} \pm 1^{\circ}\text{C}$ , calculated by taking the mean of the ductile and brittle fractures with respect to ten test specimens, has been reported in the "ambiant température impact IZOD" column. The fracture energy according to ISO standard 179 at a 10 temperature of  $23^{\circ}\text{C} \pm 1^{\circ}\text{C}$ , calculated by teking the mean of the ductile and brittle fractures with respect to ten test specimens, has been reported in the "ambient temperature impact CHARPY".  
The fracture energy according to ISO standard 179 at 15 a temperature of  $- 40^{\circ}\text{C} \pm 1^{\circ}\text{C}$ , calculated by taking the mean of the ductile and brittle fractures with respect to ten test specimens, has been reported in the "cold impact, CHARPY" column.

COMPOSITION	IMPACT ADDITIVE		CHARPY IMPACT	
	Source (Example)	Content (phr)	Fracture energy (KJ/m <sup>2</sup> )	% of DUCTILE Fracture
1	1	7	34.2	60
2	1	7.5	>52	100
3	3	7	48	100
4	3	7.5	>52	100
5	4	7	46.5	100
6	4	7.5	>52	100
7	2	7	43.1	80
8	2	8	52	100
9(c)	6	7	15.7	0
10(a)	6	8	48.6	90
11(a)	7	7	12.4	0
12(c)	7	7.5	39	70
13	8	7	15.2	0
14	8	7.5	>51	100
15	9	7	>43	100
16	9	7.5	>52	100

TABLE 1

COMPOSITION	IMPACT ADDITIVE		LOW-TEMPERATURE IMPACT	
	Source (example)	Content (phr)	Temperature of the test (in °C)	Fracture Energy (in KJ/m <sup>2</sup> )
17	1	6	-10	23.1
			-20	19.5
			-30	11.5
			-40	9.1
18	3	6	-10	22.6
			-20	20.8
			-30	5
			-40	-
19	4	6	-10	25.6
			-20	19.6
			-30	8.2
			-40	2.4
20	5	6	-10	25.9
			-20	19.3
			-30	7.6
			-40	4.6
21(c)	7	6	-10	18
			-20	17
			-30	5.4
			-40	2.5
22(c)	6	6	-10	22
			-20	15
			-30	5.1
			-40	2.1

TABLE 2

IMPACT ADDITIVE	AMBIENT TEMPERATURE	COLD IMPACT
	IMPACT (kJ/m <sup>2</sup> )	(kJ/m <sup>2</sup> )
PBT *	69,3	11,3
Example 10	62	16,1
Example 11	56,8	8,4
Example 12	74	8,8

TABLE 3

\* COMPOSITION BASED ON PBT (WITHOUT IMPACT ADDITIVE)

5

IMPACT ADDITIVE	AMBIENT TEMPERATURE	AMBIENT	COLD IMPACT,
	IMPACT IZOD (kJ/m <sup>2</sup> )	TEMPERATURE IMPACT CHARPY (kJ/m <sup>2</sup> )	CHARPY (kJ/m <sup>2</sup> )
PVDF *	7,5	8	3,7
Example 10	62,8	78,2	15,6
Example 11	49,3	60,3	11,1

TABLE 4

\* COMPOSITION BASED ON PVDF (WITHOUT IMPACT ADDITIVE)

From a review of the examples and the specification, it is clear that the core is of two types: with a covering composition and without a covering composition. When with a covering composition, said core contains 5 above zero, preferably at least 5%, more preferably at least 10%, by weight of the covering composition, with the preferred maximum percentage being about 80% by weight.

Also, the preceding examples can be repeated with 10 similar success by substituting the generically or specifically described reactants and/or operating conditions of this invention for those used in the preceding examples.

The entire disclosure of all applications, patents 15 and publications, cited above and below, and of corresponding French 95/12706, are hereby incorporated by reference.

From the foregoing description, one skilled in the art can easily ascertain the essential characteristics of 20 this invention, and without departing from the spirit and scope thereof, can make various changes and modifications of the invention to adapt it to various usages and conditions.

In this specification and the following claims, the 25 expression "ranging from 7 to 9," e.g., from 5 to 12 and the like includes values x and y, e.g., 5 and 12. Also, the abbreviation "m.g." represents meter-gram(s).

CLAIMS

1. Impact additive of the core/shell type composed of a core based on alkyl or on a polyorganosiloxane rubber and a shell based on poly(alkyl methacrylate), or on a styrene-acrylonitrile copolymer, characterized in that the said impact additive comprises from:

a) 70% to 90% by weight of a crosslinked elastomeric core which is composed:

10 1) of 20% to 100% by weight, and preferably of 20% to 90%, of a nucleus composed of a copolymer (I) of n-alkyl acrylate, the alkyl group of which has a carbon number ranging from 5 to 12, or of a mixture of alkyl acrylates, the linear or branched alkyl group of which has a carbon number ranging from 2 to 12, or of a polyorganosiloxane rubber, of a polyfunctional crosslinking agent possessing unsaturated groups in its molecule, at least one of which is of  $\text{CH}_2=\text{C}<$  vinyl type, and optionally of a polyfunctional grafting agent

15 20 possessing unsaturated groups in its molecule, at least one of which is of  $\text{CH}_2=\text{CH}-\text{CH}_2-$  allyl type, the said nucleus containing a molar amount of crosslinking agent and optionally of grafting agent ranging from 0.05% to 5%,

25 2) of 80% to 0% by weight, and preferably of 80% to 10%, of a covering composed of a copolymer (II) of n-alkyl acrylate, the alkyl group of which has a carbon number ranging from 4 to 12, or of a mixture of alkyl acrylate as defined above in 1) and

of a grafting agent possessing unsaturated groups in its molecule, at least one of which is of  $\text{CH}_2=\text{CH}-\text{CH}_2$ -allyl type, the said covering containing a molar amount 5 of grafting agent ranging from 0.05 % to 2.5 %,

b) 30 % to 10 % by weight of a shell grafted onto the said core composed of a polymer of an alkyl methacrylate, the alkyl group of which has a carbon number ranging from 1 to 4, or alternatively of a 10 statistical copolymer of an alkyl methacrylate, the alkyl group of which has a carbon number ranging from 1 to 4, and of an alkyl acrylate, the alkyl group of which has a carbon number ranging from 1 to 8, containing a molar amount of alkyl acrylate ranging 15 from 5 % to 40 %, or alternatively composed of a styrene-acrylonitrile copolymer.

2. Impact additive according to Claim 1, characterized in that the said impact additive comprises from:

20 a) 75 % to 85 % of a crosslinked elastomeric core,

b) 25 % to 15 % of a shell grafted onto the said core.

3. Impact additive according to either of 25 Claims 1 and 2, characterized in that the alkyl group of the n-alkyl acrylate of the copolymer (I) has a carbon number ranging from 5 to 8 and that the alkyl group of the n-alkyl acrylate of the copolymer (II) has

a carbon number ranging from 4 to 8.

4. Impact additive according to one of  
Claims 1 to 3, characterized in that the alkyl group of  
the alkyl acrylates of the mixture, forming part of the  
5 copolymers (I) and/or (II) has a carbon number ranging  
from 4 to 8.

5. Impact additive according to Claim 1,  
characterized in that the crosslinking agent is chosen  
from derivatives possessing at least two double bonds  
10 of  $\text{CH}_2=\text{C}$  vinyl type.

6. Impact additive according to Claim 1,  
characterized in that the crosslinking agent is chosen  
from derivatives possessing one or a number of double  
bonds of vinyl type and at least one double bond of  
15  $\text{CH}_2=\text{CH-CH}_2$ - allyl type.

7. Impact additive according to either of  
Claims 1 and 5, characterized in that the crosslinking  
agent is 1,4-butanediol diacrylate.

8. Impact additive according to either of  
20 Claims 1 and 6, characterized in that the crosslinking  
agent is allyl acrylate or methacrylate.

9. Impact additive according to Claim 1,  
characterized in that the grafting agent is chosen from  
derivatives possessing at least two double bonds of  
25  $\text{CH}_2=\text{CH-CH}_2$ - allyl type.

10. Impact additive according to Claim 1,  
characterized in that the grafting agent is chosen from  
derivatives possessing one or a number of double bonds

of allyl type and at least one double bond of vinyl type.

11. Impact additive according to either of Claims 1 and 9, characterized in that the grafting agent is diallyl maleate.

12. Impact additive according to either of Claims 1 and 10, characterized in that the grafting agent is allyl acrylate or methacrylate.

13. Impact additive according to one of Claims 1 to 12, characterized in that the nucleus of the crosslinked core has a molar amount of crosslinking agent and optionally of grafting agent of between 0.5 % and 1.5 %.

14. Impact additive according to one of Claims 1 to 4 and 10 to 12, characterized in that the covering of the crosslinked core has a molar amount of grafting agent of between 0.5 % and 1.5 %.

15. Impact additive according to one of Claims 1 to 4, characterized in that the statistical copolymer of the shell has a molar amount of alkyl acrylate of between 10 % and 20 %.

16. Impact additive according to either of Claims 1 and 3, characterized in that the n-alkyl acrylates used to form the copolymer (I) are n-pentyl acrylate, n-hexyl acrylate, n-heptyl acrylate and n-octyl acrylate.

17. Impact additive according to one of Claims 1 to 3, characterized in that the n-alkyl

acrylates used to form the copolymer (II) are n-butyl acrylate, n-pentyl acrylate, n-hexyl acrylate, n-heptyl acrylate and n-octyl acrylate.

18. Impact additive according to Claims 16  
5 and 17, characterized in that the n-alkyl acrylate for forming the copolymers (I) and (II) is n-pentyl acrylate.

19. Impact additive according to Claims 16  
and 17, characterized in that the n-alkyl acrylate for  
10 forming the copolymers (I) and (II) is n-hexyl acrylate.

20. Impact additive according to Claims 16  
and 17, characterized in that the n-alkyl acrylate for forming the copolymers (I) and (II) is n-heptyl  
15 acrylate.

21. Impact additive according to Claims 16  
and 17, characterized in that the n-alkyl acrylate for forming the copolymers (I) and (II) is n-octyl acrylate.

20 22. Impact additive according to Claims 16  
and 17, characterized in that the n-alkyl acrylate for forming the copolymer (I) is n-octyl acrylate and that the n-alkyl acrylate for forming the copolymer (II) is n-butyl acrylate.

25 23. Impact additive according to one of Claims 1 to 3, characterized in that the linear or branched alkyl acrylates constituting the mixture of alkyl acrylates used for forming the copolymers (I)

and/or (II) are ethyl acrylate, n-propyl acrylate, n-butyl acrylate, amyl acrylate, 2-methylbutyl acrylate, 2-ethylhexyl acrylate, n-hexyl acrylate, n-octyl acrylate, n-decyl acrylate, n-dodecyl acrylate and 3,5,5-trimethylhexyl acrylate.

24. Impact additive according to Claim 23, characterized in that use is made of an amount by weight of n-alkyl acrylate at least equal to 10 % by weight of the mixture of alkyl acrylates.

10 25. Impact additive according to Claim 24, characterized in that use is made of an amount by weight of n-alkyl acrylate of between 20 % and 80 % by weight of the mixture of alkyl acrylates.

15 26. Impact additive according to one of Claims 23 to 25, characterized in that the n-alkyl acrylate is n-octyl acrylate.

27. Impact additive according to Claim 1 or 2, characterized in that the alkyl methacrylate used to form the shell is methyl methacrylate.

20 28. Thermoplastic polymer composition containing an impact additive according to any one of Claims 1 to 27.

25 29. Composition according to Claim 28, characterized in that the thermoplastic polymer is composed of one or a number of polymers of the polycondensates type, in particular polyesters, such as poly(butylene terephthalate), polyamides, polyesteretheramides, polycarbonates and alloys of the

abovementioned polymers.

30. Composition according to Claim 28, characterized in that the thermoplastic polymer is composed of one or a number of polymers chosen from the 5 group formed by poly(alkyl methacrylate)s and in particular poly(methyl methacrylate); optionally superchlorinated vinyl chloride homopolymers; the copolymers which result from the copolymerization of vinyl chloride with one or a number of ethylenically 10 unsaturated comonomers and which contain at least 80 % by weight of polymerized vinyl chloride; 1,1-dichloroethylene homopolymer; or 1,1-difluoroethylene homopolymer.

31. Composition according to Claim 30, 15 characterized in that the thermoplastic polymer is a vinyl chloride homopolymer.

32. Composition according to Claim 29, characterized in that the thermoplastic polymer is a poly(butylene terephthalate).

33. Composition according to one of Claims 20 28 to 32, characterized in that the content of impact additive is between 1 part and 30 parts by weight per 100 parts by weight of the thermoplastic polymer used.

34. Composition according to Claim 33, 25 characterized in that the content of impact additive is between 5 parts and 10 parts by weight per 100 parts by weight of the thermoplastic polymer used.

35. Process for producing an impact additive

according to claim 1 comprises the preparation, in a first stage, of a crosslinked elastomeric core composed of a nucleus and of a covering and then, in a second stage, the grafting onto the said crosslinked elastomeric core of a shell made of poly(alkyl methacrylate).  
5

36. Composition according to claim 30, characterized in that the thermoplastic polymer is a 1,1-trifluoroethylene homopolymer.

10 37. An impact additive according to claim 1, wherein the core contains above 0 to 80% by weight of said covering.

38. An impact additive according to claim 37, wherein the covering constitutes at least 5% by weight of said core.

15 39. An impact additive according to claim 37, wherein the covering constitutes at least 10% by weight of said core.

40. An impact additive according to claim 1, wherein the core does not contain a covering.

IMPACT ADDITIVE OF THE CORE/SHELL TYPE  
FOR THERMOPLASTIC POLYMERS

Abstract

5 The invention relates to an impact additive of  
the core/shell type for thermoplastic polymers.

This impact additive comprises a crosslinked  
elastomeric core based on n-alkyl acrylate and a shell  
made of poly(alkyl methacrylate) grafted onto the said  
core.

**COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY**  
(Includes Reference to PCT International Applications)

ATTORNEY'S DOCKET NUMBER  
ATOCM-67

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole Inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

Impact Additive of the Core/Shell Type for Thermoplastic Polymers

the specification of which (check only one item below):

is attached hereto.

was filed as United States application

Serial No. 08/738,768

on October 28, 1996

and was amended

on October 28, 1996 (if applicable).

was filed as PCT international application

Number \_\_\_\_\_

on \_\_\_\_\_

and was amended under PCT Article 19

on \_\_\_\_\_ (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, §1.56(a).

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT International application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed:

**PRIOR FOREIGN/PCT APPLICATION(S) AND ANY PRIORITY CLAIMS UNDER 35 U.S.C. 119:**

COUNTRY (If PCT, indicate "PCT")	APPLICATION NUMBER	DATE OF FILING (day, month, year)	PRIORITY CLAIMED UNDER 35 USC 119
France	95/12706	27 October 1995	<input checked="" type="checkbox"/> YES <input type="checkbox"/> NO
			<input type="checkbox"/> YES <input type="checkbox"/> NO
			<input type="checkbox"/> YES <input type="checkbox"/> NO
			<input type="checkbox"/> YES <input type="checkbox"/> NO
			<input type="checkbox"/> YES <input type="checkbox"/> NO

**Combined Declaration For Patent Application and Power of Attorney (Continued)**  
 (Includes Reference to PCT International Applications)

ATTORNEY'S DOCKET NUMBER  
**ATOCM 67**

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) or PCT international application(s) designating the United States of America that is/are listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in that/those prior application(s) in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56(a) which occurred between the filing date of the prior application(s) and the national or PCT international filing date of this application.

U.S. APPLICATION NUMBER	U.S. FILING DATE	PATENTED	PENDING	ABANDONED
PCT APPLICATION NO.	PCT FILING DATE	U.S. SERIAL NUMBERS ASSIGNED (if any)		

**POWER OF ATTORNEY:** As a named inventor, I hereby appoint I. William Millen (19,544); John L. White (17,748); Anthony J. Zeleno (27,969); Alan E. J. Branigan (20,585); John R. Moses (24,983); Harry B. Shubin (32,004); Brion P. Heaney (32,542); Diana Hamlet-King (33,302); Richard J. Traverso (30,595); Richard E. Kurtz (33,936); John A. Sopp (33,103); Richard M. Lebovitz (37,087) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith.

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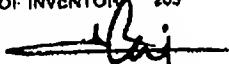
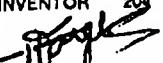
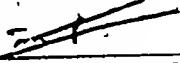
**Combined Declaration For Patent Application and Power of Attorney (Continued)**  
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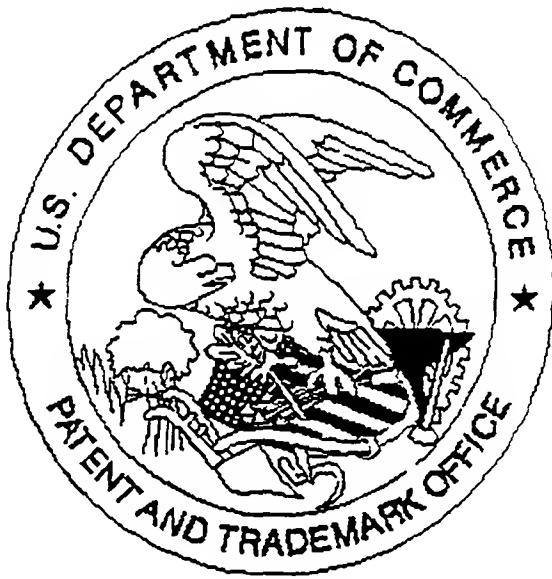
207	FAMILY NAME	FIRST GIVEN NAME	SECOND GIVEN NAME
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	STREET	CITY	STATE & ZIP CODE/COUNTRY
208	FAMILY NAME	FIRST GIVEN NAME	SECOND GIVEN NAME
	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP
	STREET	CITY	STATE & ZIP CODE/COUNTRY
209	FAMILY NAME	FIRST GIVEN NAME	SECOND GIVEN NAME
	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP
	STREET	CITY	STATE & ZIP CODE/COUNTRY
210	FAMILY NAME	FIRST GIVEN NAME	SECOND GIVEN NAME
	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP
	STREET	CITY	STATE & ZIP CODE/COUNTRY
211	FAMILY NAME	FIRST GIVEN NAME	SECOND GIVEN NAME
	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP
	STREET	CITY	STATE & ZIP CODE/COUNTRY
212	FAMILY NAME	FIRST GIVEN NAME	SECOND GIVEN NAME
	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP
	STREET	CITY	STATE & ZIP CODE/COUNTRY

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1011 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

SIGNATURE OF INVENTOR 201	DATE	SIGNATURE OF INVENTOR 207	DATE
	2-21-97		
SIGNATURE OF INVENTOR 202	DATE	SIGNATURE OF INVENTOR 208	DATE
	2/5/97		
SIGNATURE OF INVENTOR 203	DATE	SIGNATURE OF INVENTOR 209	DATE
	6/2/97		
SIGNATURE OF INVENTOR 204	DATE	SIGNATURE OF INVENTOR 210	DATE
	2/5/97		
SIGNATURE OF INVENTOR 205	DATE	SIGNATURE OF INVENTOR 211	DATE
	2/5/97		
SIGNATURE OF INVENTOR 206	DATE	SIGNATURE OF INVENTOR 212	DATE

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## Application deficiencies found during scanning:

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